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**Plant responses to simulated carbon
capture and transport leakage: the effect of impurities in the CO₂ gas
stream.**

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Running Title

Impurities in the CO₂ gas stream

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Key Words: extreme CO₂, soils, gas exchange, SO₂, H₂S, crops, soil pH, carbon capture and
storage, CCS

Abstract To deliver an effective transition from a carbon-based to a carbon-free energy market, bridging technologies are required. One such possibility is the use of carbon capture and storage, (CCS). However, before such innovations can be rolled out a key requirement is to understand the environmental impact of these technologies. Recent experimental work has demonstrated that small scale CO₂ leakage from CCS pipeline infrastructure has a localised and possibly transient impact. However, what remains unknown is the possibility of synergistic impact of impurities in the CO₂ gas stream. Here we report the impact of two impurities SO₂ (100 ppm SO₂ in pure CO₂) and H₂S (80ppm H₂S in pure CO₂) on the growth and performance of two crop species (spring wheat, *Triticum aestivum* and beetroot, *Beta vulgaris*) in fully replicated experiments. Our data show that when compared to CO₂-only gassed controls, the impact of these impurities are minimal as there are no statistically significant differences between performance parameters (photosynthesis, stomatal conductance and transpiration) or biomass. These results signify that from a plant health perspective it may not be necessary to completely remove these specific impurities prior to CO₂ transportation.



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Introduction

Many high CO₂ emitting industries (e.g. power stations) in the UK are distant from potential carbon storage sites (offshore geological reservoirs) and therefore an infra-structure of CO₂ transportation must be initiated to carry the CO₂ to safe storage. As such there is a need to understand the risks involved and mitigation of potential leaks associated with CCS and dense-phase CO₂ transportation networks into the environment. Recent experimental work has highlighted that the effects of CO₂ leakage on vegetation are highly localised (e.g. Zhou et al., 2013, Sharma et al., 2014, see Smith et al., 2016) and transient with recovery of vegetation close to complete after 12 months (Smith et al., 2016) and that stress is induced by direct CO₂ exposure in addition to a function of O₂ depletion (Lake et al., 2016).

There are, however, two largely unresolved issues; firstly is the role played by both soil type and soil structure in mitigating and/ or enhancing observed plant stresses and secondly, the effects of impurities such as SO₂ and H₂S that may be present in the CO₂ gas stream. Here we address the second issue namely that of impurities in the gas stream.

Impurities in the CO₂ gas stream are a consequence of the specific combusted fuels and capture technologies (Porter et al., 2015). Impurities not only act on the transport properties of the gas stream (Skaugen et al., 2016) but in the event of leakage into the soil environment, will impact on vegetation (including crop plants) growing above the pipeline. The range of impurities and potential concentrations within a pure CO₂ gas stream include both biologically toxic and non-toxic compounds all of which can impact on transportation processes. Non-toxic impurities include H₂O and O₂ (Brown et al., 2014, Porter et al., 2015)

and are not detrimental to plants at normal levels in the soil. However, some are known to adversely affect vegetation e.g. SO_x and NO_x when present in atmospheric pollution.

Atmospheric loading of these gases reduces the ability of plants to tolerate other abiotic stress factors. For example, the freezing tolerance of heather (*Calluna vulgaris*) is adversely affected by long-term experimental fumigation of SO₂ (plus NO₂) at a concentration of 40 nl l⁻¹ (40 ppb) (Caporn et al., 2000); and when *in situ* tolerant plants surrounding a lignite-based thermal power station in the Chennai region of India were monitored for chlorophyll, water content and pH of leaves under constant SO₂ values of 13 to 18 µg m⁻³ (13 to 18 ppb) (Govindaraju et al., 2012), all three parameters were reduced suggesting that stress is experienced under constant air pollution associated with coal combustion. H₂S has been studied more extensively and is now thought to be involved in biochemical signalling in plants, primarily by priming the biochemical defence responses to abiotic stress, comprehensively reviewed by Lisjak et al., (2013).

Studies specifically involving the soil or root environment are very few in this particular context, Christou et al. (2013) demonstrated the priming ability in strawberry to enhance tolerance to salt stress by subjecting roots to H₂S treatment in hydroponic systems. They found no effect of H₂S on chlorophyll fluorescence, stomatal conductance or water content of leaves compared to non-treated controls, while Cheng et al. (2013) found beneficial effects of H₂S for root protection during extreme hypoxia events in *Pisum sativum*, again in hydroponic systems.

To date there have been no studies into the effects on vegetation of SO₂ and H₂S as components in a CO₂ gas stream delivered directly into the soil environment. To address

these knowledge gaps we build on recent experimental protocols (Lake et al., 2016) to test for differences in plant stress as a function of impurities within a pure CO₂ stream.

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Materials and methods

Experimental setup

99 Soil chambers were constructed of acrylic plastic with pipe inlets to allow CO₂ gassing of the
soil environment exclusively. The experimental system was housed in a controlled
environment growth facility (UNIGRO, UK) to standardise the following environmental
102 variables: irradiance was 300 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (at plant height), day/night as 12/12 hours;
temperature 21/18°C; and relative humidity 60%. Gas was supplied from either an integral
supply (pure CO₂) or a gas cylinder and separated prior to entering each individual soil
105 chamber by two flow rate step-down manifolds. Gas was delivered to each individual
chamber at a rate of 30 (± 15) mL min⁻¹ to maintain CO₂ at steady state. Gases were exhausted
to the atmosphere via a separate manifold to prevent build up within the growth room. In all
108 experiments gas concentrations (CO₂ and O₂) were measured daily using the GEOTECH
GA5000 gas analyser (Geotech, Warwickshire, UK).

111 *CO₂ impurities*

To examine the specific effects that impurities within the CO₂ stream may have on plant
responses to simulated CCS leakage certified custom gas mixes were used (manufactured and
114 supplied by BOC, UK). The effect of SO₂ was studied using a mix of 100 ppm SO₂ in pure
CO₂ and H₂S using 80ppm H₂S in pure CO₂. These values were derived as midrange values
for these impurities present in the gas stream from different carbon capture technologies

(Table 1). To test for specific effects of the impurities, treatment plants ($\text{CO}_2 + \text{SO}_2$ or $\text{CO}_2 + \text{H}_2\text{S}$) were compared to treatment CO_2 - only gassed control plants.

Crop species

Crop plants used were spring wheat (*Triticum aestivum* v Tybault - a monocotyledon, grass) and beetroot (*Beta vulgaris* v Pablo F1 - a dicotyledon, vegetable). Crops were sown and grown in Levington's no. 3 multipurpose compost within an environmental controlled growth room (details above) for 1 to 2 weeks before being transplanted into the soil chambers. They were then left to allow sufficient root growth before gassing commenced (approximately 2 weeks later). The gassing period lasted for up to 5 days. After that time, plants become pot-bound which affects physiology and no longer reflects field conditions, hence the experiment was terminated. : Replication consisted of four control plants gassed with CO_2 and six plants gassed with $\text{CO}_2 + \text{H}_2\text{S}$ and six plants gassed with $\text{CO}_2 + \text{SO}_2$.

Biomass (shoot)

Plants were harvested between and at the end of each experiment. All shoots (leaves and stems) were taken from each plant, weighed, then dried at 80°C for 2 days and re-weighed. Biomass was measured as fresh and dry weight.

Plant gas exchange

Gas exchange parameters (photosynthesis (A), stomatal conductance (g_s) and evaporation (E) are a measure of plant performance under experimental conditions and determines both the ability of plants to acquire carbon and the rate of simultaneous water loss. Measurements

were made using a Li-Cor 6400x IRGA (Li-Cor Inc, Lincoln, Nebraska, USA) on each

141 replicate plant prior to and then daily during gassing until harvest.

Soil pH

144 Samples were dried at $40 \pm 4^\circ\text{C}$ and pH determined following the method of Taylor et al.,
(2005).

147 All statistical analyses were carried out using Minitab v 12 (USA). Student's t-tests of each
treatment from each other (comparison of means).

150 **Results**

CO₂ concentrations

Comparisons between impurity plus CO₂ experiments and pure CO₂ experiments indicate that
153 levels of CO₂ and O₂ are similar across all experiments (Table 2).

Biomass

156 Fig 1 shows the biomass measurements of wheat (A & B) and beetroot (C & D) when
compared to CO₂ gassed control plants. In all measured parameters there is no statistically
significant additional effect of added impurities compared to CO₂ gassed controls.

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Gas exchange

Fig 2 shows gas exchange parameters (A , g_s and E) of wheat and Fig 3 of beetroot compared to CO_2 gassed controls. All parameters are affected within the first day of gassing manifested as a dramatic reduction. Photosynthetic rate (A) is less affected than both g_s and E . Species differences are apparent with SO_2 causing greater reductions on A in wheat than H_2S while H_2S has a greater effect on A than SO_2 on A in beetroot. Although there are no significant differences between CO_2 gassed control plants and those with added impurities, Table 3 more clearly illustrates the differences in response of each species when the effect of impurities is calculated as a % of CO_2 -gassed control plants. Both respond with a slight decrease in overall biomass with addition of H_2S (black outline), while plant performance parameters are differentially affected; wheat is adversely affected by SO_2 (dashed outline) and beetroot by H_2S (black outline). Fig 4 shows the correlations of stomatal conductance (A), transpiration rate (B) and photosynthetic rate (C) with CO_2 concentrations during each experiment. There is a much stronger correlation with CO_2 concentration and both g_s and E (water loss) than with A (carbon gain).

Soil pH

Table 4 shows the pH of soil prior to growing plants and the experimental treatments along with post-gassing (experimental end). In all cases, the pre-gassed compost is significantly more acidic than with plants and gasses ($p = <0.01$, Student's t-test of means). Soil in the wheat experiment with SO_2 added is significantly more acidic than with CO_2 alone ($p = 0.013$, Student's t-test of means).

Discussion

CO₂ concentrations (and O₂-depletion) are comparable for both sets of experiments. As the impurities are mixed within the CO₂ gas stream, uniformity of impurity is delivered throughout. Biomass data is consistent with previous studies of CO₂ gassing alone (Lake et al., 2016a) and provides evidence that there is no additional effect on productivity when SO₂ or H₂S are present within the CO₂ gas stream. Gas exchange data suggest the mechanism as a disruption to water relations measured as g_s and E as evidenced by much stronger correlations between CO₂ concentration and both g_s and E (water loss) than with A (carbon gain) (Fig 4). This is commensurate with previous studies using this system which demonstrated that the main effect of CO₂ gassing is to reduce stomatal conductance with consequent loss of stomatal control (Lake et al 2016b). However, again there is no additional effect from impurities added to the CO₂ gas stream. While all gas exchange parameters are considerably reduced under CO₂ gas alone compared to non-gassed plants (Lake et al 2016a), species responses to each impurity are evident. Table 3 shows the % change in plants under CO₂ + SO₂ and CO₂ + H₂S from CO₂ gassed control plants. Although the changes are small, and not statistically significant, when calculated as % change SO₂ shows slight increases in biomass measurements, compared to H₂S which shows slight decreases. Gas exchange parameters are reduced under SO₂ in wheat, whereas they are reduced under H₂S in beetroot. This suggests that different stress mechanisms may be employed by different species in response to different impurities and importantly that all impurities cannot be assumed to produce the same results.

Soil pH (Table 4) of the compost before adding the crop plant and prior to gassing is significantly lower than after the experiments illustrating the ability of plants to influence their soil environment and raise pH to a more favourable level. Plants achieve this by producing root exudates to counter or increase acidity dependent on soil conditions as well as

influence interactions with other organisms (Wang et al., 2016, Sarker & Karmoker 2016,
Bais et al., 2006). Only under CO₂ + SO₂ in wheat does the soil become significantly lower in
pH than CO₂ gassing alone, however, this is still above the pH of pre-gassed compost, and
did not translate into any additional impact on biomass.

Conclusions

For the first time our data demonstrate that trace amounts of impurities SO₂ and H₂S in pure
CO₂ that are likely to be entrained within a CCS CO₂ stream have a negligible impact on
plant functional biology (at least under these experimental conditions) when compared to
plants exposed to pure CO₂. Therefore these data imply that from a plant health perspective it
may not be necessary to completely remove these specific impurities at concentrations tested
prior to transportation.

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Figure legends:

Figure 1. Growth characteristics of wheat grown with CO₂ + SO₂ (A), CO₂ + H₂S (B) and beetroot grown with CO₂ + SO₂ (C), CO₂ + H₂S (D) compared to pure CO₂ control after 4 to 5 days treatment. Wheat: leaf height, leaf no., tiller no., fresh weight and dry weight of all top growth (leaf material) and % moisture of all top growth. Beet fresh weight and dry weight of all top growth (leaf material) and % moisture of all top growth [n= 4 to 6, bar = SEmean].

Figure 2. Comparison of time course gas exchange measurements for wheat treated with CO₂ (control) or CO₂ + impurity (SO₂ or H₂S). Stomatal conductance (g_s), transpiration rate (E) and photosynthetic rate (A) pre-gassing (day 0) and subsequent daily measurement during gassing. [n = 4 or 6, bar = SEmean].

Figure 3. Comparison of time course gas exchange measurements for beetroot treated with CO₂ (control) or CO₂ + impurity (SO₂ or H₂S). Stomatal conductance (g_s), transpiration rate

(E) and photosynthetic rate (A) pre-gassing (day 0) and subsequent daily measurement during
gassing. [n = 4 or 6, bar = SEmean].

Figure 4. Correlations of gas exchange parameters with CO₂ concentration. All individual
points inclusive of CO₂ control and CO₂ + impurities. (A) Stomatal conductance; $R^2 = 0.79$;
(B) Transpiration rate; $R^2 = 0.84$; (C) photosynthetic rate $R^2 = 0.38$; (Solid line is the linear
regression and the dotted line the 95% confidence intervals around the regression, n = 10)

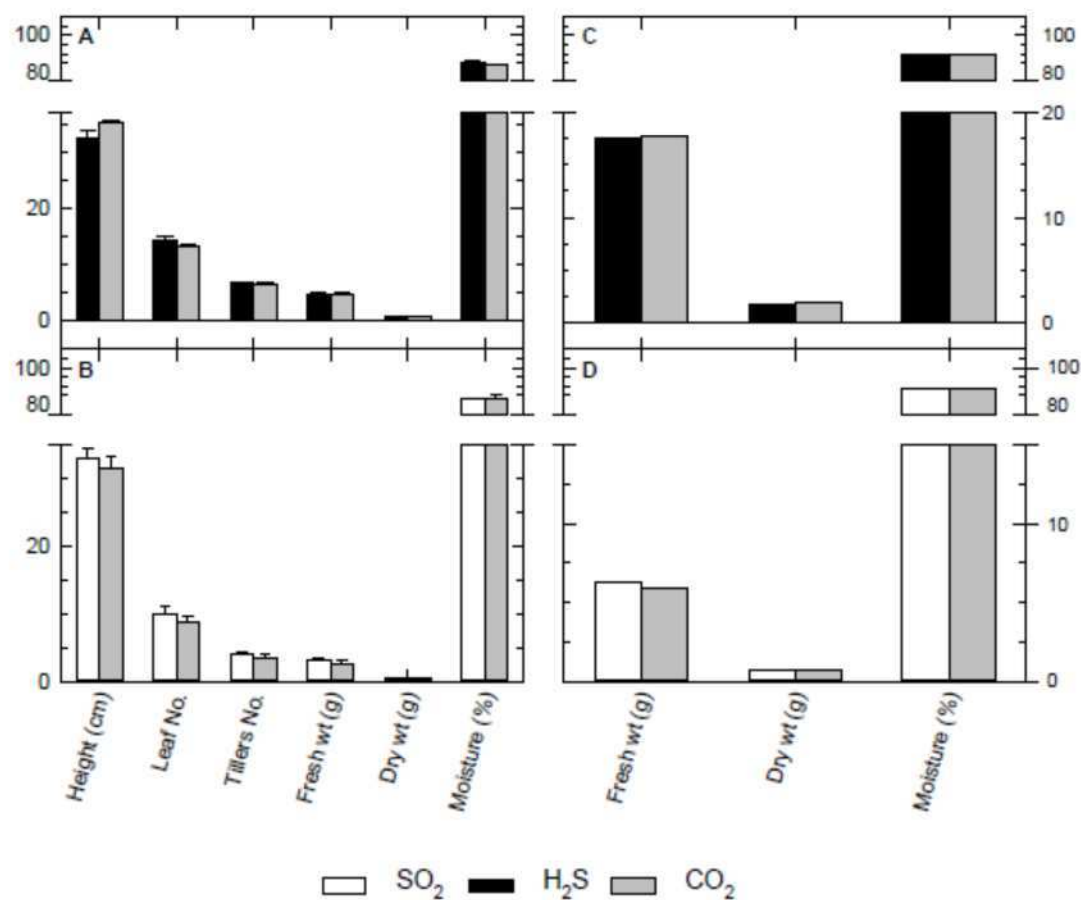


Figure 1

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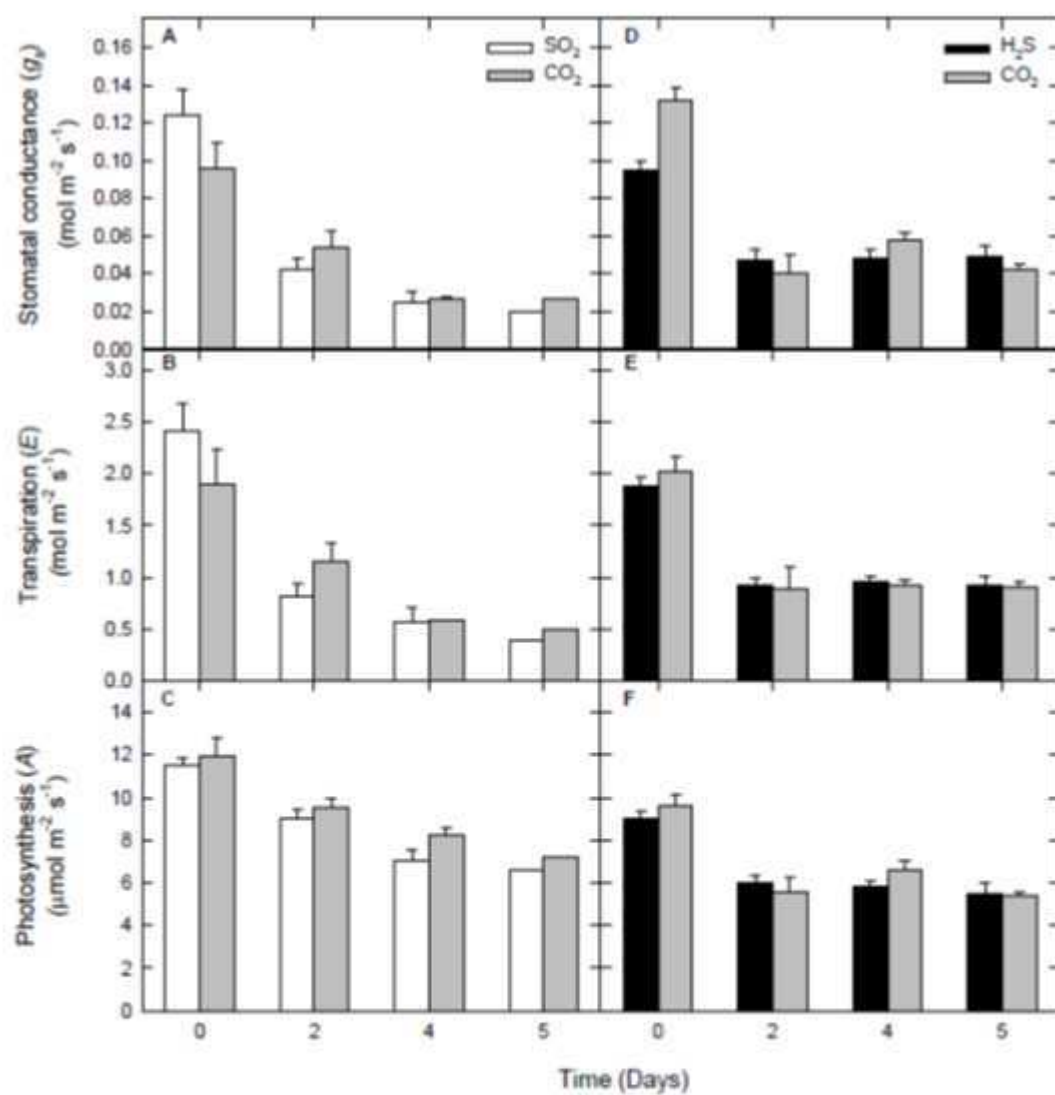


Figure 2

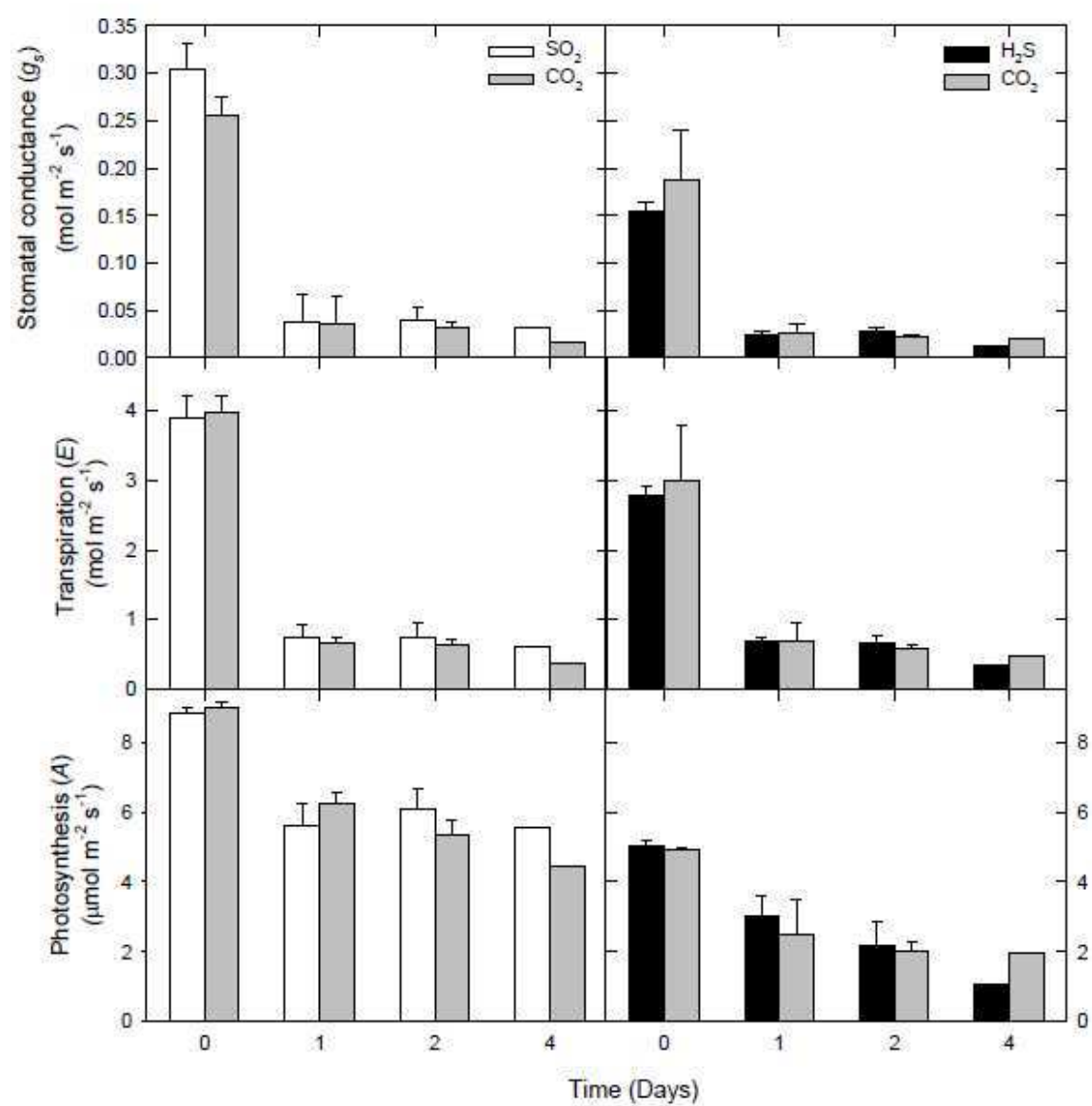


Figure 3

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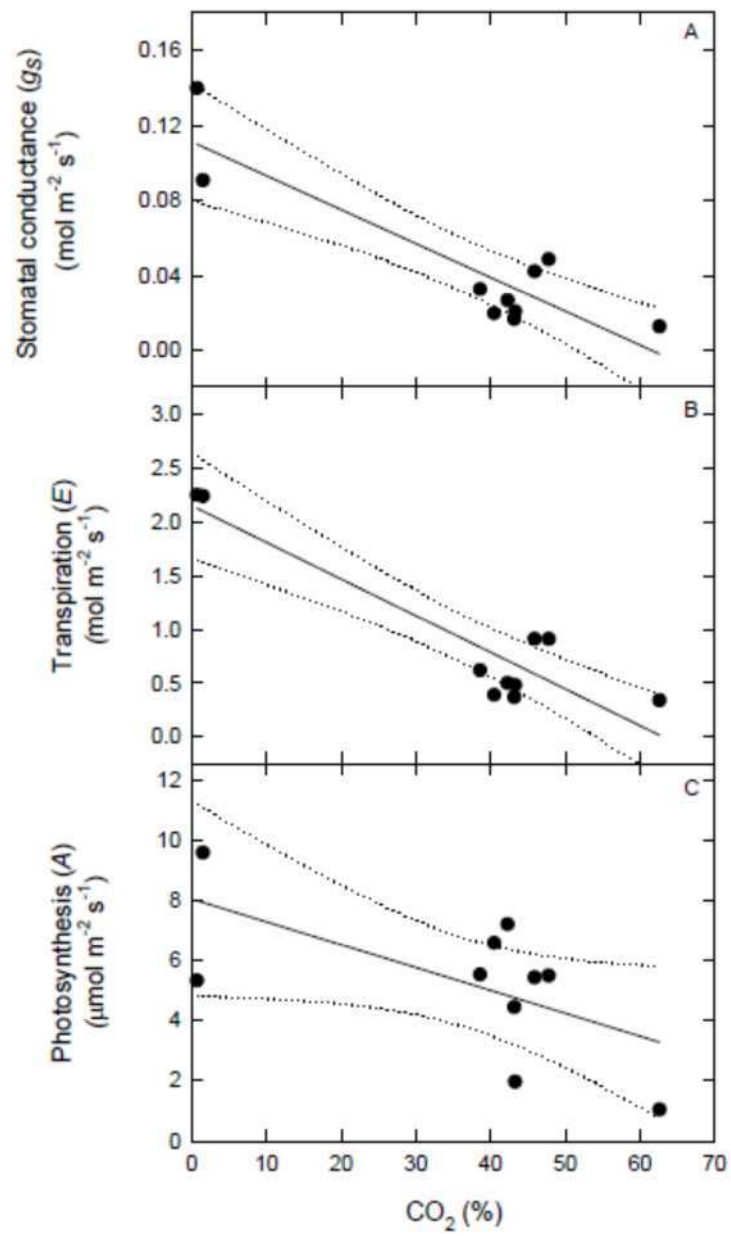


Figure 4

Table 1. Range of concentrations of specific impurities (SO₂, H₂S) in the CO₂ gas stream from different capture technologies

339		Oxy-fuel combustion			pre-combustion	post-combustion
		Raw/	double	distillation		
		dehumidified	flashing			
342	CO ₂ % v/v	74.8-85	95.8-96.7	99.3-99.4	95-99	99.6-99.8
	SO ₂ ppmv	50-100	0-4500	37-50	25	0-61.7
	H ₂ S/COS ppmv				0-34000	
345	Adapted from Brown et al 2014; COS = carbonyl sulphide					

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Table 2. Mean gas concentrations measured as % CO₂ and % O₂ within the soil chambers.

351	Crop and impurity	CO ₂ concentration (%)		O ₂ concentration (%)	
		CO ₂ gassed	CO ₂ + impurity	CO ₂ gassed	CO ₂ + impurity
	Wheat				
354	SO ₂	42.3 (1.2)	40.5 (0.34)	11.0 (0.36)	12.1 (0.09)
	H ₂ S	45.9 (2.08)	47.8 (5.83)	10.5 (0.30)	10.2 (0.38)
357	Beetroot				
	SO ₂	43.2 (2.54)	38.6 (3.93)	11.4 (0.48)	12.3 (2.48)
	H ₂ S	43.3 (1.79)	62.6 (3.64)	11.3 (0.34)	7.3 (0.38)
360	[n = 3 for pure CO ₂ , 5 for CO ₂ + impurity; (SEmean)]				

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375 **Table 3.** Percentage change in biomass and gas exchange parameters from CO₂-gassed control plants (black outline = H₂S effect, dashed outline = SO₂ effect). Data from the controls are actual values.

378	Crop and impurity	Biomass		gas exchange parameters		
		fresh weight (g)	dry weight (g)	photosynthetic rate (A)	stomatal conductance (g _s)	transpiration (E)
	Wheat					
381	SO ₂ added	+18.6	+6.25	-8.86	-25.19	-22.48
	Control for SO ₂ (CO ₂ only)	2.57	0.42	7.217	0.027	0.503
	H ₂ S added	-1.23	-11.25	+1.12	+16.1	+0.44
384	Control for H ₂ S (CO ₂ only)	4.88	0.77	5.435	0.042	0.907
	Beetroot					
387	SO ₂ added	+6.08	+4.61	+24.12	+87.7	+66.8
	Control for SO ₂ (CO ₂ only)	5.92	0.64	1.972	0.0215	0.476
	H ₂ S added	-1.01	-6.81	-47.08	-35.39	-28.67
390	Control for H ₂ S (CO ₂ only)	17.77	1.9	4.458	0.174	0.374

393 **Table 4.** Mean soil pH [n = 3 for CO₂ only, n = 5 for CO₂ + impurity, letters denote
significant difference, see text].

Crop and impurity		soil pH		
		pre-gassed	CO ₂ gassed	CO ₂ + impurity
Wheat				
	SO ₂	5.23 ^a	5.61 ^b	5.45 ^c
399	H ₂ S	5.23 ^a	5.45 ^b	5.49 ^b
Beetroot				
402	SO ₂	5.34 ^a	5.41 ^b	5.61 ^b
	H ₂ S	5.34 ^a	5.63 ^b	5.61 ^b

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